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Jean-Luc Dubois et al.) Group Art Unit: 1621
Application No.: 10/526,877) Examiner: KARL J. PUTTLITZ
Filed: September 6, 2005) Confirmation No.: 5557
For: METHOD FOR THE PRODUCTION OF)
ACRYLIC ACID FROM PROPANE, IN)
THE PRESENCE OF MOLECULAR)
OXYGEN)

SUBMISSION OF VERIFIED ENGLISH TRANSLATION OF PRIORITY DOCUMENT

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

Attached is a verified English translation of French Patent Application No. 02 11 197, filed September 10, 2002, from which the present application claims the benefit of priority provided in 35 U.S.C. § 119.

In the Office Action mailed August 18, 2006, The Examiner acknowledged receipt of a copy of the certified copy of the French priority application forwarded by the International Bureau.

Respectfully submitted,

BUCHANAN INGERSOLL & ROONEY PC

Date: June 20, 2007

By:

T.D. Boone
Travis D. Boone
Registration No. 52635

P.O. Box 1404
Alexandria, VA 22313-1404
703 836 6620

HIRSCH

&

ASSOCIES

AVOCATS AU BARREAU DE PARIS

European Patent Attorneys (EPA)

Community Trademark Attorneys (CTA)

Marc-Roger Hirsch EPA - CTA
Ingénieur ENSCS - Licencié es Sciences Physiques

Gérard-Gabriel Lamoureux CTA
Docteur en Droit - Spécialiste Propriété Intellectuelle

Grégoire Desrousseaux EPA - CTA
Ingénieur Ecole Polytechnique & ENS Telecom

Louis-Bernard Buchman DEA
New York Bar - Spéc. Droit Communautaire

AVOCATS AU BARREAU DE PARIS

Elizabeth Simpson-Karzja CTA - LLB London

Jean-Marc Lefrançois DESS Droit U.E.

Claire de Chassey

Etienne Glorian L.Droit Lausanne - DESS P.I. - CTA

Privat Vigand EPA - CTA - Ingénieur Supélec

Docteur en Droit

Heike Blum Rechtsanwältin Munich Bar

Denis Schertenleib PhD Molecular Biology

Solicitor Law Society of England and Wales

Elisabeth de Morelos CTA

Pierre-Alexis Leray Ingénieur Supélec

MSc. Georgia Tech. - DESS P.I.

Aviva Leszczynski DEA Droit des Affaires

Emmanuel Adda New York Bar - LL.M Boston

Liliane Hoffmann DEA P.I.

CONSULTANTS
Maîtres en Droit

François Pochart EPA

Ingénieur Ecole Polytechnique & ENSIC

Sylvain Hirsch CTA

Emmanuelle Tévenin DESS P.I. - CTA

Yves Reinhardt EPA

Ingénieur ENSAIS - DEA Droit Privé

Grégoire Ingrand CTA

Sophie Marc DESS P.I.

Loïc Depelley EPA - Ingénieur HEI

Anne-Sophie Schaefer

Ingénieur ENSAT (Agronomie)

Marie Ahin Docteur en Droit

Benjamin Mouche DEA P.I.

Jean Baptiste Sirand DESS P.I.

Alexandre Varlik DESS (IT Law)

CONSULTANTS
Ingénieurs

Michel Rochet EPA - CTA

Jean Claude Vieillefosse EPA

Michael Robinson

Maryse Dugast-Zrihen CEIPI

Sébastien Ragot CEIPI

Françoise Lobjois CEIPI

Murielle Khairallah EPA

Frédéric Nguyen

Sophie Galdeano

Pierre Cortey EPA - CTA

Michel Rubinstein

In the matter of United States
Patent Application
10/526,877

DECLARATION

I, Michael Bevan Robinson, of Cabinet Hirsch & Associés, 58 avenue Marceau, 75008 Paris, France hereby declare that I am well acquainted with the English and French languages and that the following is to the best of my knowledge and belief a true and accurate translation of the text of French patent Application 02 11 197 filed on September 10, 2002, publication No. 2,844,263 entitled

METHOD FOR THE PRODUCTION OF ACRYLIC ACID FROM PROPANE, IN THE PRESENCE OF MOLECULAR OXYGEN, and attached hereto, which is the priority application for said United States Patent Application 10/526,877.

And I declare this to be true and correct and I understand that willful false statements and the like are punishable by fine or imprisonment or both, under 18 U.S.C. 1001.

Signature



Date May 16, 2007

**METHOD FOR THE PRODUCTION OF ACRYLIC ACID FROM
PROPANE, IN THE PRESENCE OF MOLECULAR OXYGEN**

The present invention relates to the production of acrylic acid from propane
5 in the presence of molecular oxygen.

It is known from European patent application No. EP-A-608838 to prepare an unsaturated carboxylic acid from an alkane according to a catalytic oxidation reaction in vapour phase in the presence of a catalyst containing a mixed metal oxide comprising as essential components, Mo, V, Te, O, as well as at least one element
10 chosen from the group constituted by niobium, tantalum, tungsten, titanium, aluminium, zirconium, chromium, manganese, iron, ruthenium, cobalt, rhodium, nickel, palladium, platinum, antimony, bismuth, boron, indium and cerium, these elements being present in very precise proportions. The reaction can be implemented using a gaseous mixture composed of the alkane, oxygen, an inert gas and water
15 vapour corresponding to the following molar proportions:

alkane/oxygen/inert gas/water vapour = 1/0.1-10/0-20/0.2-70 and preferably
1/1-5/0-10/5-40.

Moreover, the European patent application No. EP-A-895809 describes catalysts based on oxides comprising molybdenum, vanadium, niobium, oxygen, tellurium and/or antimony, as well as at least one other element such as iron or aluminium. These catalysts can be used for the conversion of propane to acrylic acid, in the presence of molecular oxygen, as illustrated in Examples 9 and 10. Example 9, in particular, describes the oxidation of propane using a catalyst of formula $Mo_1V_{0.33}Nb_{0.11}Te_{0.22}O_n$ from a gas flow composed of propane, oxygen, helium and a
20 flow of water vapour, according to a molar ratio propane/oxygen/helium/water vapour of approximately 1/3.2/12.1/14.3. In such a gas flow, the flow of reactive gas has a very low concentration of propane. Consequently the recycling of the unconverted propane is much more difficult because this unconverted propane is too
25 diluted in the reaction flow.

30 The aim of the invention is to propose a method for the production of acrylic acid from propane, in the presence of molecular oxygen, which allows a higher conversion of propane to be obtained while retaining good acrylic acid selectivity.

35 The inventors have discovered that this aim can be achieved by passing a gaseous mixture of propane, oxygen and water vapour, and if appropriate an inert gas, over a particular catalyst, under conditions such that the oxygen of the gaseous mixture is in a substoichiometric proportion in relation to the propane introduced, which probably allows the catalyst to act in a similar way to a redox system and

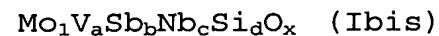
provides the oxygen which is lacking so that the reaction is carried out in a satisfactory way.

The advantages of this novel method are the following:-

- the limitation of the overoxidation of the products formed which takes place in the presence of too great a quantity of molecular oxygen; according to the present invention, due to the fact of operating in substoichiometry, the formation of CO_x (carbon monoxide and carbon dioxide), degradation products, is reduced, which allows the acrylic acid selectivity to be increased;
- 10 - the acrylic acid selectivity is maintained at a good level;
- the conversion is increased without loss of selectivity;
- the catalyst undergoes only a low reduction and therefore a small loss of its activity; it can easily be regenerated by heating in the presence of oxygen or a gas containing oxygen after a certain period of use; after regeneration, the catalyst regains its initial activity and can be used in another reaction cycle;
- 15 - moreover, the separation of the stages of reduction of the catalyst and of regeneration of the latter can be provided which allows the partial pressure of propane to be increased, such a partial supply pressure of propane being little limited by the existence of an explosive zone created by the propane + oxygen mixture, because the later is present in molecular form in substoichiometric proportions;
- 20 - moreover, this method allows reduction of the formation of products produced by hydration, in particular propionic acid, acetone and acetic acid.
- 25

The subject of the present invention is therefore a method for the production of acrylic acid from propane, in which a gaseous mixture containing propane, molecular oxygen, water vapour as well as, if appropriate, an inert gas, is passed over a catalyst of formula (I) or the formula (Ibis):

30



in which:

- a is comprised between 0.006 and 1, inclusive;
- 35 - b is comprised between 0.006 and 1, inclusive;
- c is comprised between 0.006 and 1, inclusive;
- d is comprised between 0 and 3.5, inclusive; and

- x is the quantity of oxygen bound to the other elements and depends on their oxidation state.

in order to oxidize the propane to acrylic acid, this method being characterized in that the molar ratio propane/molecular oxygen in the initial gaseous mixture is greater than 0.5.

Such a method allows an acrylic acid selectivity to be obtained of close to 60 % and a high conversion of propane. Moreover, it can easily be implemented in a fluidized bed or in a moving bed and the injection of the reagents can be carried out at different points of the reactor, so as to be outside of the flammability zone while having a high propane concentration and, consequently, a high catalyst productivity.

According to a particularly advantageous embodiment, the method according to the invention comprises the following stages:

- a) the gaseous mixture is introduced into a first reactor with a moving catalyst bed;
- 15 b) at the outlet of the first reactor, the gases are separated from the catalyst;
- c) the catalyst is returned into a regenerator;
- d) the gases are introduced into a second reactor with a moving catalyst bed;
- 20 e) at the outlet of the second reactor, the gases are separated from the catalyst and the acrylic acid contained in the separated gases is recovered;
- f) the catalyst is returned into the regenerator; and
- g) the regenerated catalyst from the regenerator is reintroduced into the first and second reactors;

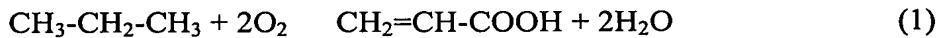
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Other characteristics and advantages of the invention will now be described in detail in the following description which is given with reference to the single attached figure which diagrammatically represents an apparatus which is suitable for the implementation of an advantageous embodiment of the method according to the invention.

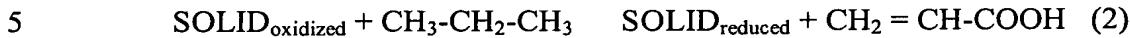
DETAILED DESCRIPTION OF THE INVENTION

According to the invention, because the molar ratio propane/molecular oxygen in the initial gaseous mixture is greater than 0.5, the conversion of the propane to acrylic acid using the catalyst is carried out by oxidation, probably according to the following concurrent reactions (1) and (2):

- the standard catalytic reaction (1):



- and the redox reaction (2):



The propane/water vapour volume ratio in the initial gaseous mixture is not critical and can vary within wide limits.

Similarly, the proportion of inert gas, which can be helium, krypton, a mixture of these two gasses, or nitrogen, carbon dioxide, etc., is also not critical and can also vary within wide limits.

The proportions of the constituents of the initial gaseous mixture are generally as follows (in molar ratios):

propane/oxygen/inert(He-Kr)/H₂O (vapour) =

15 1/0.05-2/1-10/1-10

Preferably, they are 1/0.1-1/1-5/1-5.

Yet more preferably, they are 1/0.167-0.667/2-5/2-5. As particularly beneficial proportions the following may also be cited:

1/0.2-0.4/4-5/4-5.

Generally, reactions (1) and (2) are carried out at a temperature of 200 to 500°C, preferably from 250 to 450°C, yet more preferably from 350 to 400°C.

The pressure in the reactor is generally from 1.01×10^4 to 1.01×10^6 Pa (0.1 to 10 atmospheres), preferably from 5.05×10^4 to 5.05×10^6 Pa (0.5-5 atmospheres).

25 The residence time in the reactor, or if there are several, in each reactor, is generally from 0.01 to 90 seconds, preferably from 0.1 to 30 seconds.

Regarding the catalyst, this corresponds to the formula (I) or the formula Ibis:

30 $\text{Mo}_{1-x}\text{V}_a\text{Te}_b\text{Nb}_c\text{Si}_d\text{O}_x$ (I) $\text{Mo}_{1-x}\text{V}_a\text{Sb}_b\text{Nb}_c\text{Si}_d\text{O}_x$ (Ibis):

in which:

- a is comprised between 0.006 and 1, inclusive;
 - b is comprised between 0.006 and 1, inclusive;
 - c is comprised between 0.006 and 1, inclusive;
 - d is comprised between 0 and 3.5, inclusive; and
 - x is the quantity of oxygen bound to the other elements and depends on oxidation state.

Advantageously:

- a is comprised between 0.09 and 0.8, inclusive;
- b is comprised between 0.04 and 0.6, inclusive;
- c is comprised between 0.01 and 0.4, inclusive; and
- d is comprised between 0.4 and 1.6, inclusive.

5

The oxides of the different metals included in the composition of the catalyst of formula (I) can be used as raw materials in the preparation of this catalyst, but the raw materials are not limited to the oxides; as other raw materials, there may be mentioned:

10

- in the case of molybdenum, ammonium molybdate, ammonium paramolybdate, ammonium heptamolybdate, molybdic acid, molybdenum halides or oxyhalides such as MoCl₅, organometallic compounds of molybdenum such as molybdenum alkoxides such as Mo(OC₂H₅)₅, acetylacetone molybdenyl;

15

- in the case of vanadium, ammonium metavanadate, vanadium halides or oxyhalides such as VCl₄, VCl₅ or VOCl₃, organometallic compounds of vanadium such as vanadium alkoxides such as VO(OC₂H₅)₃;

- in the case of tellurium, tellurium, telluric acid and TeO₂;

- in the case of niobium, niobic acid Nb₂(C₂O₄)₅, niobium tartrate, niobium hydrogen oxalate, oxotrioxalatoammonium niobate {(NH₄)₃[NbO(C₂O₄)₃]•1.5H₂O}, niobium and ammonium oxalate, niobium oxalate and tartrate, niobium halides or oxyhalides such as NbCl₃, NbCl₅ and organometallic compounds of niobium such as niobium alkoxides such as Nb(OC₂H₅)₅, Nb(O-n-Bu)₅

20

25

and, generally, all the compounds which are able to form an oxide by calcination, namely, the metallic salts of organic acids, the metallic salts of mineral acids, the metal complex compounds, etc.

The source of silicon is generally constituted by colloidal silica and/or polysilicic acid.

30

According to particular embodiments, the catalyst of formula (I) can be prepared by mixing aqueous solutions of niobic acid, ammonium heptamolybdate, ammonium metavanadate, telluric acid under stirring, by the addition preferably of colloidal silica, then by precalcinating under air at approximately 300 C and by calcinating under nitrogen at approximately 600 C.

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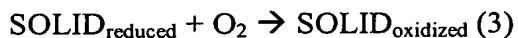
Preferably, in the catalyst of formula (I) or (Ibis):

- a is comprised between 0.09 and 0.8, inclusive;
- b is comprised between 0.04 and 0.6, inclusive;
- c is comprised between 0.01 and 0.4, inclusive; and

- d is comprised between 0.4 and 1.6, inclusive.

During the redox reaction (2), the catalyst undergoes reduction and a progressive loss of its activity. This is why, once the catalyst has at least partially changed to the reduced state, its regeneration is carried out according to reaction (3):

5



by heating in the presence of oxygen or a gas containing oxygen at a temperature of 250 to 500 C, for a time necessary for the reoxidation of the catalyst.

10 Generally the method is carried out until the reduction ratio of the catalyst is comprised between 0.1 and 10 g of oxygen per kg of catalyst.

This reduction ratio can be monitored during the reaction through the quantity of products obtained. Then the equivalent quantity of oxygen is calculated. It can also be monitored through the exothermicity of the reaction.

15 After regeneration, which can be carried out under temperature and pressure conditions which are identical to, or different from those of the reactions (1) and (2), the catalyst regains an initial activity and can be reintroduced into the reactors.

The reactions (1) and (2) and the regeneration (3) can be carried out in a standard reactor, such as a fixed bed reactor, a fluidized bed reactor or a moving bed 20 reactor.

Thus the reactions (1) and (2) and the regeneration (3) can be carried out in a device with two stages, namely a reactor and a regenerator which operate simultaneously and in which two catalyst loadings alternate periodically.

The reactions (1) and (2) and the regeneration (3) can also be carried out in 25 the same reactor by alternating the periods of reaction and regeneration.

Preferably, the reactions (1) and (2) and the regeneration (3) are carried out in a reactor with a moving catalyst bed, in particular in a vertical reactor, the catalyst then preferably moving from the bottom upwards.

A operating method with only one passage of the gas or with recycling of the 30 gas can be used.

According to a preferred embodiment, the propylene produced as a by-product and/or the propane which has not reacted are recycled (or returned) to the inlet of the reactor, i.e. they are reintroduced at the inlet of the reactor, in a mixture or in parallel with the initial mixture of propane, water vapour and if appropriate 35 inert gas or gases.

Use of an apparatus with two reactors and a regenerator

According to an advantageous embodiment of the invention, the method according to the invention is used in an apparatus such as the one represented in the attached figure.

5 The initial gaseous mixture comprising propane, molecular oxygen, water vapour as well as, if appropriate, an inert gas, is introduced into a first reactor (Riser 1) containing the moving catalyst bed.

Then, at the outlet of the first reactor, the effluents are separated into gases and the moving bed catalyst.

10 The catalyst is sent into a regenerator.

The gases are introduced into a second reactor (Riser 2) also containing a moving catalyst bed.

At the outlet of the second reactor, the effluents are separated into gases and the moving bed catalyst.

15 The catalyst is sent into a regenerator.

The gases are treated in a known way, generally by absorption and purification, with a view to recovering the acrylic acid produced.

The regenerated catalyst is reintroduced into the first reactor as well as into the second reactor.

20 The method thus operates continuously, the circulation of the catalyst between the reactors and the regenerator is carried out in a regular and generally continuous way.

Of course, the single regenerator can be replaced by two or more regenerators.

25 Moreover, it is possible to add, after the second reactor, other reactors which also have a catalyst circulating between each of these reactors and the regenerator or other regenerators.

Preferably, the first and second reactors are vertical and the catalyst is transported upwards by the gas flow.

30 A method of operating with only one passage of gases or with recycling of the products leaving the second reactor can be used.

According to a preferred embodiment of the invention, after treatment of the gas originating from the second reactor, the propylene produced as a by-product and/or the propane which has not reacted are recycled (or returned) to the inlet of the reactor, i.e. they are reintroduced at the inlet of the first reactor, in a mixture or in parallel with the initial mixture of propane, oxygen, water vapour and if appropriate of inert gas or gases.

Use of a cocatalyst

According to another advantageous embodiment of the invention, the gaseous mixture also passes over a cocatalyst.

This has the advantage of reducing the production of propionic acid, which is generally a by-product of the conversion reaction and which poses problems in certain applications of acrylic acid when it is present in too great a quantity.

Thus, the propionic acid /acrylic acid ratio is greatly reduced at the outlet of the reactor.

Moreover, the formation of acetone, which is also a by-product of the production of acrylic acid from propane, is reduced.

To this end, at least one of the reactors comprises a cocatalyst with the following formula (II):



15

in which:

- a' is comprised between 0.006 and 1, inclusive;
- b' is comprised between 0 and 3.5, inclusive;
- c' is comprised between 0 and 3.5, inclusive;
- 20 - d' is comprised between 0 and 3.5, inclusive;
- e' is comprised between 0 and 1, inclusive;
- f' is comprised between 0 and 1, inclusive;
- g' is comprised between 0 and 1, inclusive;
- h' is comprised between 0 and 3.5, inclusive;
- 25 - i' is comprised between 0 and 1, inclusive;
- j' is comprised between 0 and 1, inclusive;
- k' is comprised between 0 and 1, inclusive;
- l' is comprised between 0 and 1, inclusive;
- m' is comprised between 0 and 1, inclusive; and
- 30 - n' is comprised between 0 and 1, inclusive.

Such a cocatalyst can be prepared in the same way as the catalyst of formula (I).

The oxides of the different metals included in the composition of the cocatalyst of formula (II) can be used as raw materials in the preparation of this cocatalyst, but the raw materials are not limited to the oxides; as other raw materials, the corresponding nitrates can be mentioned in the case of nickel, cobalt, bismuth, iron or potassium.

Generally, the cocatalyst is present in the form of a moving bed and preferably it is regenerated and circulates, if appropriate, in the same way as the catalyst.

Preferably, in the cocatalyst of formula (II):

- 5 - a' is comprised between 0.01 and 0.4, inclusive;
- b' is comprised between 0.2 and 1.6, inclusive;
- c' is comprised between 0.3 and 1.6, inclusive;
- d' is comprised between 0.1 and 0.6, inclusive;
- e' is comprised between 0.006 and 0.01, inclusive.
- 10 - f' is comprised between 0 and 0.4, inclusive;
- g' is comprised between 0 and 0.4, inclusive;
- h' is comprised between 0.01 and 1.6, inclusive;
- i' is comprised between 0 and 0.4, inclusive;
- j' is comprised between 0 and 0.4, inclusive;
- 15 - k' is comprised between 0 and 0.4, inclusive;
- l' is comprised between 0 and 0.4, inclusive;
- m' is comprised between 0 and 0.4, inclusive; and
- n' is comprised between 0 and 0.4, inclusive.

The weight ratio of the catalyst to the cocatalyst is generally greater than 0.5
20 and preferably at least 1.

Advantageously, the cocatalyst is present in the two reactors.

The catalyst and the cocatalyst are present in the form of solid catalytic compositions.

They can each be in the form of pellets, generally of 20 to 300 µm in
25 diameter, the catalyst and cocatalyst pellets generally being mixed before implementation of the method according to the invention.

The catalyst and the cocatalyst can also be present in the form of a solid catalytic composition composed of pellets each of which comprises both the catalyst and the cocatalyst.

30

Examples

The following examples illustrate the present invention without limiting its scope.

In the formulae given in Example 1, x is the quantity of oxygen bound to the
35 other elements and depends on their oxidation states.

The conversions, selectivities and yields are defined as follows:

		Number of moles of propane having reacted
	Conversion (%) =	$\frac{\text{Number of moles of propane having reacted}}{\text{Number of moles of propane introduced}} \times 100$
5	Selectivity (%) for acrylic acid =	$\frac{\text{Number of moles of acrylic acid formed}}{\text{Number of moles of propane having reacted}} \times 100$
10	Yield (%) of acrylic acid =	$\frac{\text{Number of moles of acrylic acid formed}}{\text{Number of moles of propane introduced}} \times 100$
15		

The selectivities and yields relating to the other compounds are calculated in a similar way.

The conversion ratio is the weight of catalyst (in kg) required to convert 1 kg of propane.

Example 1

20 Preparation of the catalyst of formula $Mo_1V_{0.33}Nb_{0.11}Te_{0.22}Si_{0.95}O_x$

a) Preparation of a solution of niobium

640 g of distilled water then 51.2g of niobic acid (i.e. 0.304 moles of niobium) are introduced into a 5 l beaker. Then 103.2 g (0.816 moles) of dehydrated oxalic acid is added.

25 The molar ratio oxalic acid/niobium is therefore 2.69.

The solution obtained previously is heated at 60 C for 2 hours, being covered so as to avoid evaporation and with stirring. Thus a white suspension is obtained which is left to cool to 30 C under stirring, which takes approximately 2 hours.

30 b) Preparation of a solution of Mo, V and Te

2120 g of distilled water, 488 g of ammonium heptamolybdate (i.e. 2.768 moles of molybdenum), 106.4 g of ammonium metavanadate NH_4VO_3 (i.e. 0.912 moles of vanadium) and 139.2 g of telluric acid (supplier: FLUKA) (i.e. 0.608 moles of tellurium) are introduced into a 5 l beaker.

35 The solution obtained previously is heated at 60 C for 1 hour and 20 minutes, being covered so as to avoid evaporation and with stirring. In this way a clear red solution is obtained which is left to cool to 30 C under stirring, which takes approximately 2 hours.

5 c) Introduction of the silica

393.6g of Ludox silica (containing 40% by weight of silica, supplied by Dupont) is introduced under stirring into the previously prepared solution of Mo, V and Te. The latter retains its limpidity and its red colouring.

Then the previously prepared solution of niobium is added. In this way a fluorescent orange gel is obtained after stirring for a few minutes. This solution is then dried by atomization. The atomizer used is a laboratory atomizer (ATSELAB from Sodeva). The atomization takes place in a nitrogen atmosphere.

10 The working parameters are globally:

- flow rate of nitrogen of the order of 45 Nm³/h;
- flow rate of slurry of the order of 500 g/h;
 - inlet temperature of the gas comprised between 155°C and 170°C;
 - outlet temperature of the gas comprised between 92°C and 100°C.

15 Then the product recovered (355.2g), which has a particle size less than 40 microns, is placed in an oven overnight at 130 C, in a teflon-covered plate.

In this way 331 g of dry product is obtained.

20 d) Calcination

The precalcinations and calcinations were carried out under air and nitrogen flow in steel capacitors. These capacitors are directly installed in muffle furnaces and the air is supplied via the flue. An internal thermometer well allows precise monitoring of the temperature. The cover is useful to prevent air returning towards the catalyst.

25 Firstly, the 331g of precursor obtained previously are precalcinated for 4 hours at 300 C under air flow of 47.9ml/min/g of precursor.

The solid obtained is then calcinated for 2 hours at 600°C under a nitrogen flow of 12.8 ml/min/g of solid.

In this way the desired catalyst is obtained.

30

Example 2

Catalyst tests

a) Apparatus

35 In order to simulate the method according to the invention, simulations were carried out in a laboratory fixed bed reactor, by generating propane pulses and oxygen pulses.

The following are loaded from the bottom to the top of a vertical reactor with cylindrical shape and made of pyrex:

- a first height of 1 ml of silicon carbide in the form of particles of 0.125 mm in diameter,
- a second height of 1 ml of silicon carbide in the form of particles of 0.062 mm in diameter,
- 5 - a third height of 5 g of catalyst in the form of particles of 0.02 to 1 mm diluted with 10 ml of silicon carbide in the form of particles of 0.062 mm in diameter,
- a fourth height of 1 ml of silicon carbide in the form of particles of 0.062 mm in diameter,
- 10 - a fifth height of 3 ml of silicon carbide in the form of particles of 0.125 mm in diameter and
- a sixth height of silicon carbide in the form of particles of 1.19 mm in diameter so as to fill all of the reactor.

15 b) Operating method

The reactor is then heated to 250 C and the vaporiser to 200 C. The electric initiation of the water pump is actuated.

Once the reactor and the vaporiser have reached the temperatures given above, the water pump is actuated and the temperature of the reactor is raised to the 20 desired test temperature, i.e. 400 C.

The hot spot of the reactor is then left to stabilize for 30 minutes.

Then, oxygen is introduced in 10 pulses of 23 seconds each in order to sufficiently oxidize the catalyst. The catalyst is considered to be totally oxidized when the temperature of the hot spot has stabilized, i.e. when there is no more 25 exothermal activity due to the reaction (by monitoring the catalyst temperature measured using a thermocouple placed in the catalyst bed, the fluctuations in temperature can be seen as a function of the pulses).

The pressure at the inlet of the reactor was approximately 1.1 to 1.8 bars (absolute) and the pressure drop across the reactor is approximately 0.1 to 0.8 bars 30 (relative).

Test A

- The production of acrylic acid was measured using a redox balance.
- 35 - A redox balance is composed of 40 redox cycles. A redox cycle represents:
 - 10 cycles of:

- 30 seconds of propane + 5 seconds of oxygen (oxygen being injected at the start of the propane pulse), with the proportions propane/O₂/He-Kr/H₂O of 10/10/45/45, with a helium-krypton flow of 4.292 N1/h (N1 = litre of gas at 0°C and 760 mm Hg);
- 5 - an intermediate pulse composed only of the flow of carrier gas He-Kr/H₂O of 45 seconds;
- an oxygen pulse with the proportions O₂/He-Kr/H₂O = 20/45/45 for 60 seconds and
 - another intermediate pulse composed only of the flow of carrier gas He-Kr/H₂O of 45 seconds;
- 10 10 cycles of:
 - 30 seconds of propane + 10 seconds of oxygen, with the proportions propane/O₂/He-Kr/H₂O of 10/10/45/45, with a flow of helium-krypton of 4.292 N1/h;
 - an intermediate pulse composed only of the flow of carrier gas He-Kr/H₂O of 45 seconds;
 - an oxygen pulse with the proportions O₂/He-Kr/H₂O = 20/45/45 for 60 seconds and
 - another intermediate pulse composed only of the flow of carrier gas He-Kr/H₂O of 45 seconds;
- 15 -10 cycles of:
 - 30 seconds of propane + 15 seconds of oxygen, with the proportions propane/O₂/He-Kr/H₂O of 10/10/45/45, with a flow of helium-krypton of 4.292 N1/h;
 - an intermediate pulse composed only of the flow of carrier gas He-Kr/H₂O of 45 seconds;
 - an oxygen pulse with the proportions O₂/He-Kr/H₂O = 20/45/45 for 60 seconds and
 - another intermediate pulse composed only of the flow of carrier gas He-Kr/H₂O of 45 seconds;
- 20 -10 cycles of:
 - 30 seconds of propane + 20 seconds of oxygen, with the proportions propane/O₂/He-Kr/H₂O of 10/10/45/45, with a flow of helium-krypton of 4.292 N1/h;
 - an intermediate pulse composed only of the flow of carrier gas He-Kr/H₂O of 45 seconds;
 - an oxygen pulse with the proportions O₂/He-Kr/H₂O = 20/45/45 for 60 seconds and
 - another intermediate pulse composed only of the flow of carrier gas He-Kr/H₂O of 45 seconds; and
- 25 -10 cycles of:
 - 30 seconds of propane + 25 seconds of oxygen, with the proportions propane/O₂/He-Kr/H₂O of 10/10/45/45, with a flow of helium-krypton of 4.292 N1/h;
 - an intermediate pulse composed only of the flow of carrier gas He-Kr/H₂O of 45 seconds;
 - an oxygen pulse with the proportions O₂/He-Kr/H₂O = 20/45/45 for 60 seconds and
 - another intermediate pulse composed only of the flow of carrier gas He-Kr/H₂O of 45 seconds; and
- 30 -10 cycles of:
 - 30 seconds of propane + 30 seconds of oxygen, with the proportions propane/O₂/He-Kr/H₂O of 10/10/45/45, with a flow of helium-krypton of 4.292 N1/h;
 - an intermediate pulse composed only of the flow of carrier gas He-Kr/H₂O of 45 seconds;
 - an oxygen pulse with the proportions O₂/He-Kr/H₂O = 20/45/45 for 60 seconds and
- 35 -10 cycles of:
 - 30 seconds of propane + 35 seconds of oxygen, with the proportions propane/O₂/He-Kr/H₂O of 10/10/45/45, with a flow of helium-krypton of 4.292 N1/h;
 - an intermediate pulse composed only of the flow of carrier gas He-Kr/H₂O of 45 seconds;
 - an oxygen pulse with the proportions O₂/He-Kr/H₂O = 20/45/45 for 60 seconds and

- another intermediate pulse composed only of the flow of carrier gas He-Kr/H₂O of 45 seconds.

During the balancing, four samples are taken, each representing 10 cycles. 4 samples of gas are also carried out using gas bags, each sample representing 5 approximately 10 cycles. (The gas samples are carried out over a period corresponding to a multiple of the duration of a cycle, in order to be able to know the theoretical quantity of propane injected).

Each small gas-washing bottle (with a 25 ml capacity and filled with 20 ml of water) is equipped with a gas bag, and when the bottle is connected to the outlet of 10 the reactor (as soon as the liquid bubbles), the bag is open and the chronometer is started.

In order to verify the oxidation state of the catalyst, another series of ten 23-second pulses of oxygen is carried out. It shows that the oxidation state of the solid has been maintained during the balancing (no exothermal activity).

15 The liquid effluents are analyzed on a HP 6890 chromatograph, after having carried out a specific calibration.

The gases are analyzed during the balancing on a Chrompack micro-GC chromatograph.

An assay of the acidity is carried out on each bottle during the operation, in 20 order to determine the exact number of moles of acid produced and to validate the chromatographic analyses.

Test B

The procedure was undertaken as in test A, except that the redox 25 balance was composed of the following 40 redox cycles:

-10 cycles of:

- 30 seconds of propane + 5 seconds of oxygen, (the oxygen being injected at the start of the propane pulse) with the proportions propane/O₂/He-Kr/H₂O of 20/15/45/45, with a flow of helium-krypton of 30 4.292 N1/h;

- an intermediate pulse composed only of the flow of carrier gas He-Kr/H₂O of 60 seconds;

- an oxygen pulse with the proportions O₂/He-Kr/H₂O = 20/45/45 for 60 seconds and

- another intermediate pulse composed only of the flow of carrier gas He-Kr/H₂O of 60 seconds;

-10 cycles of:

- 30 seconds of propane + 10 seconds of oxygen, with the proportions propane/O₂/He-Kr/H₂O of 20/15/45/45, with a flow of helium-krypton of 4.292 N1/h;
 - an intermediate pulse composed only of the flow of carrier gas He-Kr/H₂O of 60 seconds;
 - an oxygen pulse with the proportions O₂/He-Kr/H₂O = 20/45/45 for 60 seconds and
 - another intermediate pulse composed only of the flow of carrier gas He-Kr/H₂O of 60 seconds;
- 5 -10 cycles of:
- 30 seconds of propane + 15 seconds of oxygen, with the proportions propane/O₂/He-Kr/H₂O of 20/15/45/45, with a flow of helium-krypton of 4.292 N1/h;
 - an intermediate pulse composed only of the flow of carrier gas He-Kr/H₂O of 60 seconds;
 - an oxygen pulse with the proportions O₂/He-Kr/H₂O = 20/45/45 for 60 seconds and
 - another intermediate pulse composed only of the flow of carrier gas He-Kr/H₂O of 60 seconds; and
- 10 -10 cycles of:
- 30 seconds of propane + 20 seconds of oxygen, with the proportions propane/O₂/He-Kr/H₂O of 20/15/45/45, with a flow of helium-krypton of 4.292 N1/h;
 - an intermediate pulse composed only of the flow of carrier gas He-Kr/H₂O of 60 seconds;
 - an oxygen pulse with the proportions O₂/He-Kr/H₂O = 20/45/45 for 60 seconds and
 - another intermediate pulse composed only of the flow of carrier gas He-Kr/H₂O of 60 seconds; and
- 15 -10 cycles of:
- 30 seconds of propane + 20 seconds of oxygen, with the proportions propane/O₂/He-Kr/H₂O of 20/15/45/45, with a flow of helium-krypton of 4.292 N1/h;
 - an intermediate pulse composed only of the flow of carrier gas He-Kr/H₂O of 60 seconds;
 - an oxygen pulse with the proportions O₂/He-Kr/H₂O = 20/45/45 for 60 seconds and
 - another intermediate pulse composed only of the flow of carrier gas He-Kr/H₂O of 60 seconds; and
- 20 -10 cycles of:
- 30 seconds of propane + 20 seconds of oxygen, with the proportions propane/O₂/He-Kr/H₂O of 20/15/45/45, with a flow of helium-krypton of 4.292 N1/h;
 - an intermediate pulse composed only of the flow of carrier gas He-Kr/H₂O of 60 seconds;
 - an oxygen pulse with the proportions O₂/He-Kr/H₂O = 20/45/45 for 60 seconds and
 - another intermediate pulse composed only of the flow of carrier gas He-Kr/H₂O of 60 seconds; and
- 25 -10 cycles of:
- 30 seconds of propane + 5 seconds of oxygen, (the oxygen being injected at the start of the propane pulse) with the proportions propane/O₂/He-Kr/H₂O of 20/20/45/45, with a flow of helium-krypton of 4.292 N1/h;
- 30 **Test C**
- The procedure was the same as in test A, except that the redox balance was composed of the following 40 redox cycles:
- 10 cycles of:
- 30 seconds of propane + 5 seconds of oxygen, (the oxygen being injected at the start of the propane pulse) with the proportions propane/O₂/He-Kr/H₂O of 20/20/45/45, with a flow of helium-krypton of 4.292 N1/h;

- an intermediate pulse composed only of the flow of carrier gas He-Kr/H₂O of 60 seconds;
 - an oxygen pulse with the proportions O₂/He-Kr/H₂O = 20/45/45 for 60 seconds and
- 5 - another intermediate pulse composed only of the flow of carrier gas He-Kr/H₂O of 60 seconds;
- 10 cycles of:
- 30 seconds of propane + 10 seconds of oxygen, with the proportions propane/O₂/He-Kr/H₂O of 20/10/45/45, with a flow of helium-krypton of 4.292 N1/h;
 - an intermediate pulse composed only of the flow of carrier gas He-Kr/H₂O of 60 seconds;
 - an oxygen pulse with the proportions O₂/He-Kr/H₂O = 20/45/45 for 60 seconds and
- 10 - another intermediate pulse composed only of the flow of carrier gas He-Kr/H₂O of 60 seconds;
- 10 cycles of:
- 30 seconds of propane + 15 seconds of oxygen, with the proportions propane/O₂/He-Kr/H₂O of 20/6.7/45/45, with a flow of helium-krypton of 4.292 N1/h;
 - an intermediate pulse composed only of the flow of carrier gas He-Kr/H₂O of 60 seconds;
 - an oxygen pulse with the proportions O₂/He-Kr/H₂O = 20/45/45 for 60 seconds and
- 15 - another intermediate pulse composed only of the flow of carrier gas He-Kr/H₂O of 60 seconds;
- 10 cycles of:
- 30 seconds of propane + 20 seconds of oxygen, with the proportions propane/O₂/He-Kr/H₂O of 20/5/45/45, with a flow of helium-krypton of 4.292 N1/h;
 - an intermediate pulse composed only of the flow of carrier gas He-Kr/H₂O of 60 seconds;
 - an oxygen pulse with the proportions O₂/He-Kr/H₂O = 20/45/45 for 60 seconds and
- 20 - another intermediate pulse composed only of the flow of carrier gas He-Kr/H₂O of 60 seconds; and
- 10 cycles of:
- 30 seconds of propane + 20 seconds of oxygen, with the proportions propane/O₂/He-Kr/H₂O of 20/5/45/45, with a flow of helium-krypton of 4.292 N1/h;
 - an intermediate pulse composed only of the flow of carrier gas He-Kr/H₂O of 60 seconds;
 - an oxygen pulse with the proportions O₂/He-Kr/H₂O = 20/45/45 for 60 seconds and
- 25 - another intermediate pulse composed only of the flow of carrier gas He-Kr/H₂O of 60 seconds; and
- 10 cycles of:
- 30 seconds of propane + 20 seconds of oxygen, with the proportions propane/O₂/He-Kr/H₂O of 20/5/45/45, with a flow of helium-krypton of 4.292 N1/h;
 - an intermediate pulse composed only of the flow of carrier gas He-Kr/H₂O of 60 seconds;
 - an oxygen pulse with the proportions O₂/He-Kr/H₂O = 20/45/45 for 60 seconds and
- 30 - another intermediate pulse composed only of the flow of carrier gas He-Kr/H₂O of 60 seconds; and
- 10 cycles of:
- 30 seconds of propane + 20 seconds of oxygen, with the proportions propane/O₂/He-Kr/H₂O of 20/5/45/45, with a flow of helium-krypton of 4.292 N1/h;
 - an intermediate pulse composed only of the flow of carrier gas He-Kr/H₂O of 60 seconds;
 - an oxygen pulse with the proportions O₂/He-Kr/H₂O = 20/45/45 for 60 seconds and
- 35 - another intermediate pulse composed only of the flow of carrier gas He-Kr/H₂O of 60 seconds.

The procedure was the same as in test A, except that the redox balance was composed of the following 40 redox cycles:

-10 cycles of:

5 - 30 seconds of propane + 5 seconds of oxygen, (the oxygen being injected at the start of the propane pulse) with the proportions propane/O₂/He-Kr/H₂O of 30/30/45/45, with a flow of helium-krypton of 4.292 N1/h;

10 - an intermediate pulse composed only of the flow of carrier gas He-Kr/H₂O of 60 seconds;

15 - an oxygen pulse with the proportions O₂/He-Kr/H₂O = 20/45/45 for 60 seconds and

20 - another intermediate pulse composed only of the flow of carrier gas He-Kr/H₂O of 60 seconds;

-10 cycles of:

25 - 30 seconds of propane + 10 seconds of oxygen, with the proportions propane/O₂/He-Kr/H₂O of 30/15/45/45, with a flow of helium-krypton of 4.292 N1/h;

30 - an intermediate pulse composed only of the flow of carrier gas He-Kr/H₂O of 60 seconds;

35 - an oxygen pulse with the proportions O₂/He-Kr/H₂O = 20/45/45 for 60 seconds and

- another intermediate pulse composed only of the flow of carrier gas He-Kr/H₂O of 60 seconds;

-10 cycles of:

35 - 30 seconds of propane + 15 seconds of oxygen, with the proportions propane/O₂/He-Kr/H₂O of 30/10/45/45, with a flow of helium-krypton of 4.292 N1/h;

- an intermediate pulse composed only of the flow of carrier gas He-Kr/H₂O of 60 seconds;

35 - an oxygen pulse with the proportions O₂/He-Kr/H₂O = 20/45/45 for 60 seconds and

- another intermediate pulse composed only of the flow of carrier gas He-Kr/H₂O of 60 seconds; and

-10 cycles of:

35 - 30 seconds of propane + 20 seconds of oxygen, with the proportions propane/O₂/He-Kr/H₂O of 30/7.5/45/45, with a flow of helium-krypton of 4.292 N1/h;

- an intermediate pulse composed only of the flow of carrier gas He-Kr/H₂O of 60 seconds;
- an oxygen pulse with the proportions O₂/He-Kr/H₂O = 20/45/45 for 60 seconds and
- 5 - another intermediate pulse composed only of the flow of carrier gas He-Kr/H₂O of 60 seconds;

c) Results

10 The final results correspond to the microbalances carried out on the 4 gas-washing bottles and the 4 gas bags.

In tests A and B, the quantity of oxygen injected was increasing when changing from one series of 10 cycles to another, because the duration of the oxygen pulse was increasing.

15 In tests C and D, the quantity of oxygen remained constant when changing from one series of 10 cycles to another. In fact, although the duration of the oxygen pulse increased from one series of 10 cycles to another, the proportion of oxygen in the pulse was adjusted (reduced) each time.

The results are compiled in the following Tables I and II:

TEST	A	B	C	D
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In the reaction:
propane+oxygen / He-Kr/H₂O
10+10/45/45 20+15/45/45 20+(20/10/6.7/5)45/45 30+(30/15/10/7.5)45/45

Selectivities (%)

Duration of the oxygen pulses injected into the propane pulses	5	10	15	20	5	10	15	20	5	10	15	20	5	10	15	20
Acrylic acid	45.2	48.6	50.1	56.2	39.9	41.6	45.8	49.0	35.0	35.9	31.7	28.2	33.9	35.1	29.1	28.6
Acetic acid	10.7	8.9	10.2	8.1	10.9	9.9	8.7	8.9	11.9	12.2	13.1	13.6	12.8	12.9	14.8	16.0
Acrolein	0.16	0.15	0.15	0.15	0.12	0.10	0.10	0.10	0.08	0.08	0.08	0.08	0.09	0.09	0.09	0.09
Acetone	0.58	0.53	0.52	0.51	0.81	0.67	0.58	0.54	0.78	0.74	0.81	0.78	0.96	1.00	1.14	1.24
Propionic acid	0.24	0.28	0.25	0.22	0.22	0.21	0.20	0.21	0.96	0.22	0.21	0.33	0.66	0.23	0.25	
Allyl alcohol	0.04	0.06	0.08	0.06	0.03	0.03	0.04	0.02	0.02	0.02	0.01	0.02	0.02	0.02	0.02	
Allyl acrylate	0.00	0.09	0.10	0.11	0.04	0.10	0.04	0.10	0.00							
Propyl aldehyde	0.00															
Acetaldehyde	0.05	0.00	0.00	0.04	0.04	0.04	0.03	0.04	0.04							
CO	15.3	15.1	14.4	12.8	16.1	16.1	15.6	15.1	17.7	16.8	18.2	19.0	15.6	15.0	16.4	15.7
CO₂	15.9	14.7	12.8	11.4	18.1	17.1	15.4	13.5	20.0	19.2	21.0	23.1	18.3	17.8	20.0	19.9
Propylene	11.8	11.6	11.4	10.4	13.7	14.2	13.5	12.4	14.2	14.1	14.8	15.1	18.0	17.3	18.3	18.1
Selectivity in acrylic acid	45.2	48.6	50.1	56.2	39.9	41.6	45.8	49.0	35.0	35.9	31.7	28.2	33.9	35.1	29.1	28.6
Selectivity in acrylic acid and propylene	57.0	60.2	61.5	66.6	53.5	55.8	59.2	61.4	49.2	50.0	46.6	43.3	51.9	52.5	47.3	46.7

TABLE II

TEST	A				B				C				D			
In the reaction: propane+oxygen / He- KrH ₂ O	10+10/45/45				20+15/45/45				20+(20/10/6.75)45/45				30+(30/15/10/7.5)45/45			
Selectivities (%)																
Duration of the oxygen pulses injected into the propane pulses	5	10	15	20	5	10	15	20	5	10	15	20	5	10	15	20
Yields (%)																
Acrylic acid	11.75	13.05	14.04	16.73	9.14	9.54	11.16	12.99	7.84	8.15	6.95	6.07	6.55	7.06	5.59	5.52
Acetic acid	2.77	2.40	2.85	2.41	2.51	2.26	2.13	2.37	2.67	2.76	2.87	2.92	2.48	2.59	2.84	3.10
Acrolein	0.04	0.04	0.04	0.05	0.03	0.02	0.02	0.03	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Acetone	0.15	0.14	0.15	0.15	0.19	0.15	0.14	0.14	0.17	0.17	0.18	0.17	0.19	0.20	0.22	0.24
Propionic acid	0.06	0.07	0.08	0.07	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.06	0.13	0.05	0.05
Allyl alcohol	0.01	0.02	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.00
Allyl acrylate	0.00	0.02	0.03	0.03	0.01	0.02	0.01	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Propyl aldehyde	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Acetaldehyde	0.01	0.00	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
CO	3.98	4.06	4.04	3.82	3.70	3.68	3.80	4.01	3.96	3.81	3.98	4.08	3.00	3.02	3.15	3.04
CO ₂	4.14	3.94	3.59	3.41	4.15	3.93	3.76	3.58	4.48	4.37	4.60	4.96	3.53	3.58	3.84	3.85
Propylene	3.06	3.12	3.19	3.09	3.13	3.25	3.28	3.28	3.18	3.20	3.25	3.26	3.47	3.49	3.51	3.50
Propane	73.55	72.65	71.76	69.72	77.20	77.14	75.55	73.59	77.69	77.38	78.21	78.44	80.63	79.89	80.88	80.73
Carbon balance (%)	99.53	99.52	99.79	99.49	100.12	100.09	99.92	100.09	100.09	100.10	100.10	99.98	99.93	99.99	100.11	100.06
Quantity of oxygen consumed (g O/kg catalyst)	1.64	1.73	1.79	1.88	2.77	2.85	2.97	3.18	2.77	2.84	2.85	2.89	3.59	3.79	3.71	3.70
μmole propane for 1 cycle	390	406	412	417	735	767	769	732	752	762	764	1162	1184	1178	1175	
μmole O ₂ added per cycle	53	107	160	214	107	214	320	427	107	107	107	107	161	161	161	161
μmole O consumed (products formed)/cycle	511	542	559	589	865	891	929	994	867	889	892	902	1122	1184	1158	1157
Propane conversion ratio (kg catalyst/kg propane converted)	1058	1023	991	924	650	649	606	561	678	669	694	701	495	477	502	498

From Table I above the following observations can be drawn:

- in the same test A or B, the larger the quantity of oxygen injected, the higher the acrylic acid selectivity;
- tests C and D show that it is better to have a high partial pressure of oxygen for a short time than the same quantity of oxygen for a longer time.

5 From Table II the following observations can be drawn:

- 10 - the quantity of oxygen consumed, calculated on the basis of the products formed, does not increase much with the addition of molecular oxygen and the conversion does not change much with the addition of molecular oxygen;
- the quantity of oxygen consumed (in μ moles of atomic oxygen) is greater than the quantity added by the pulse; this means that the catalyst was reduced in any case;
- 15 - the conversion is higher in Test A.